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AIR QUALITY SURVEY (TAGA 3000)
NORTHERN WOOD PRESERVERS INC.,
THUNDER BAY, JUNE 1989

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NORTHERN WOOD PRESERVERS INC., THUNDER BAY

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Executive Summary

At the request of the Northwestern Region, the mobile TAGA 3000 unit of the Ministry's Air Resources Branch conducted an air quality survey in Thunder Bay on June 10, 11, 12, 14, 15, 16 and 17, 1989. The survey objective was to chemically "fingerprint" the odours associated with Northern Wood Preservers Inc. (NWP) and to determine the ambient concentrations of phenols, chlorophenols and polycyclic aromatic hydrocarbons (PAHs) downwind of NWP.

The survey crew noted tar odours downwind of NWP on each monitoring day. The intensity of this odour ranged from mild to strong. Analysis of the mass spectra of ambient air samples taken downwind of NWP provided evidence for the following contaminants: toluene, phenol, xylenes, benzaldehyde, cresols, C_3-alkyl benzenes, dibutylamine and PAH groups namely, $C_{10}H_8$ (naphthalene), $C_{11}H_{10}$ (methylnaphthalene), $C_{12}H_{10}$ (biphenyl), $C_{12}H_{12}$ (ethylnaphthalene), $C_{13}H_{10}$ (fluorene) $C_{13}H_{14}$ (trimethylnaphthalene) and $C_{14}H_{10}$ (anthracene).

Low levels of phenol and cresol were detected; phenolic odours were not readily evident. Concentration estimates of phenol ranged from non-detected to 9 $\mu g/m_3$ and, of cresol from non-detected to 5 $\mu g/m^3$ which are well below the Ministry standards of 100 and 230 $\mu g/m^3$, respectively. Chlorophenols were not detected during any of the monitoring periods.

The PAH group $C_{10}H_8$, most likely naphthalene, was the most abundant. Half-hour average concentrations of naphthalene, in residential areas directly downwind of NWP, are in the range 7.4 to 52 $\mu g/m^3$. Three of the 25 half-hour averages indicated that naphthalene levels exceeded the Ministry guideline of 36 $\mu g/m^3$. Approximately half of the readings showed naphthalene levels of about 20 $\mu g/m^3$. Half-hour average concentration levels of the PAH groups $C_{11}H_{10}$, $C_{12}H_{10}$ and $C_{13}H_{10}$ (probably methylnaphthalene, biphenyl, fluorene) were in the range 0.3 to 17 $\mu g/m^3$. The Ministry guideline for biphenyl, based on odours, is 60 $\mu g/m^3$. There is no Ministry standard or guideline for methylnaphthalene or fluorene. It is recommended that the Northwestern Region consider the implementation of a detailed PAH monitoring programme in the vicinity of NWP to determine the impact of PAHs on the local air quality.

Table of Contents

1.0 Introduction 1

2.0 The TAGA "Fingerprinting" Technique 2
  2.1 Survey Strategy 3

3.0 Results and Discussion 4
  June 10 4
  June 11 5
  June 12 6
  June 14 6
  June 15 7
  June 16 8
  June 17 9

4.0 Summary and Conclusions 9

5.0 Acknowledgements 11

Appendix A 20

Appendix B 21

Appendix C 22

List of Figures

Map 1: Monitoring Locations Downwind of Northern Wood Preservers Inc. 12
Figure 1: Plume Tracking Profile 18
Figure 2: Real-time measurements of Four PAH Groups 19

List of Tables

Table 1: Monitoring Periods and Locations Downwind of NWP 13
Table 2: Mobile TAGA Odour "Fingerprints" Downwind of NWP 14
Table 3: Mobile TAGA Quantitative Half-Hour Average Concentrations of four PAH groups downwind of NWP 16

1.0 Introduction

At the request of the Northwestern Region of the Ontario Ministry of the Environment, the Air Resources Branch conducted a mobile air monitoring survey in the vicinity of Northern Wood Preservers Inc. (NWP) in Thunder Bay, Ontario, during June, 1989. The Northwestern Region expressed special interest in the odours originating from wood preserving processes at the NWP plant. Thus, the purpose of the survey was to chemically "fingerprint" any odours emanating from NWP, and to determine ambient levels of phenol, cresols, chlorophenols and polycyclic aromatic hydrocarbons (PAHs). Mobile Air Monitoring Unit (MAMU) #3, containing a TAGA 3000 mass spectrometer, was used for fingerprinting and quantitation of major contaminants.

The Northern Wood Preservers Inc. is located on the shoreline of Lake Superior, in the City of Thunder Bay. The NWP complex includes a slasher, a tie sawmill, a lumber sawmill, three drying kilns and two treatment plants. There are two areas used for wood preserving: a treatment facility which uses chromated copper arsenate, and a three retort treatment area where wood is treated with creosote (retorts #1 and #2) and pentachlorophenol (retort # 3). Tar odours are mainly noticeable at times when treated wood is removed from the creosote retorts. Utility poles, railway ties and guard rail posts are treated with creosote or pentachlorophenol. Retort cylinder #1 was opened, to remove treated wood, 8 times during the survey period, retort cylinder #2 was opened 9 times, and retort cylinder #3 was used only once.

A detailed description of NWP's wood preserving process is provided in Appendix C, along with the operating status and schedules of the pertinent processes during the survey period.

Presented here is the analysis of air samples acquired downwind of Northern Wood Preservers Inc. as determined in the field by the mobile TAGA 3000 unit on June 10, 11, 12, 14, 15, 16 and 17, 1989.

2.0 The TAGA "Fingerprinting" Technique

The Trace Atmospheric Gas Analyser (TAGA) model 3000 is a specialized single quadrupole mass spectrometer with a unique air sampling inlet system and ion source which operates at atmospheric pressure. Ambient air is sampled continuously at a high flow rate (100 l/min.) directly into the ionization chamber, where various classes of contaminants are selectively ionized via appropriate chemical ionization (CI) reagents added to the flowing air sample. For example, atmospheric water vapour highlights ketones, aldehydes, alcohols and acids, ammonia highlights amines, amides and some ethers, benzene highlights aromatics and sulphurous species, and oxygen highlights phenols, chlorophenols and acids.

The ionization of pollutants yields a mixture of pseudo-molecular ions which are immediately subjected to mass analysis up to 250 amu (atomic mass units). Mass "fingerprinting" is achieved in approximately 20 minutes if all four CI reagents are employed. The chemical or pollutant fingerprint arises from the interpretation of all of the mass spectra for a given monitoring period. Since the analysis of TAGA 3000 data is based on mass spectral interpretation, the resultant chemical identifications are somewhat tentative, the degree of uncertainty depending on the sample composition.

Owing to the system's unique feature of direct air sampling, and atmospheric chemical ionization, the technique is highly sensitive to many polar organic pollutants in real-time. In general, the TAGA can detect volatile compounds which contain a heteroatom such as N, O, P, S, or halide. Typical real-time detection limits for the TAGA are in the range of 0.1 to 10 $\mu g/m^3$, depending on the type of chemical(s) and the complexity of the sample matrix.

Real-time quantitation of PAHs is achieved using a unique ionization method in the APCI source of the TAGA systems. In the positive ion mode PAHs are detected as molecular ions via charge transfer reactions initiated by molecular benzene ions. For example, naphthalene is observed as $C_{10}H_8^+$. The TAGA 3000 provides information on individual PAH groups, not specific isomers. Calibration of the TAGA response to volatile PAHs is accomplished by injecting known amounts of PAHs via a motorized syringe drive directly into the sample air stream. For this particular survey, a benzene solution containing naphthalene, 2-methylnaphthalene, biphenyl and fluorene, was used for calibrating the TAGA response to the $C_{10}H_8$, $C_{11}H_{10}$, $C_{12}H_{10}$ and $C_{13}H_{10}$ PAH groups. With the exception of June 10, the TAGA 3000 was calibrated three times for naphthalene, methylnaphthalene, biphenyl and fluorene responses over the concentration range of 0 to 60, 0 to 120, 0 to 60 and 0 to 25 $\mu g/m^3$, respectively, a minimum of once daily. No other compounds were calibrated; however, their concentrations were estimated from previous studies of such compounds. Appendix A lists the daily average TAGA responses to four PAHs. Average detection limits for naphthalene, methylnaphthalene, biphenyl and fluorene as determined during the survey were approximately 1, 0.4, 0.4 and 0.2 $\mu g/m^3$, respectively.

2.1 Survey Strategy

Basically, the survey strategy was to position the mobile TAGA unit downwind of the source of interest during an odour episode and acquire air quality data. Since one of the objectives of this survey was to chemically characterize any odours, mass spectral data were recorded at times when odours were noticeable and persistent. Four CI reagents (H_2O, NH_3, C_6H_6, O_2) were used for detection of different classes of compounds. Ideally odours must be present for at least 20 minutes, the time it takes to complete the fingerprinting process. Monitoring locations were selected using the following criteria:

1) wind direction and wind speed;
2) plume tracking (real-time target compound measurements while mobile)
3) presence of odours
4) type of chemicals detected (fingerprint)
5) road network and accessibility.

Wind speed and wind direction data, collected at a height of 10 meters, were displayed by the on-board computer system and updated every 30 seconds. The meteorological data ensured that the monitoring locations were indeed downwind of the source of interest. Easterly winds were a prerequisite for monitoring the emissions and odours from NWP. Often it was necessary to wait for the "right" wind directions so that meaningful data could be obtained.

Plume tracking refers to the real-time determination of the instantaneous concentrations of PAHs while the TAGA unit was driven in the vicinity of the alleged source. Provided the winds are steady and the PAH levels above background levels, plume tracking can immediately reveal the highest ground level concentrations and the "best" monitoring locations.

In addition to downwind (source) monitoring, fingerprint mass scans were also acquired at locations upwind of NWP (background). The source data was then background-corrected by simply subtracting the upwind signals from the downwind signals for each amu. The net signal is attributed to the source, provided the wind direction is appropriate.

3.0 Results and Discussion

The mobile TAGA 3000 unit conducted ambient air monitoring in Thunder Bay on June 10, 11, 12, 14, 15, 16 and 17, 1989. A total of 17 fingerprints of the ambient air were determined at a number of locations downwind of Northern Wood Preservers Inc. Monitoring was conducted near the NWP property and in residential areas west of Ft. William Road and Water Street (See Map 1). Table 1 summarizes the survey activities in terms of downwind monitoring periods, sampling locations, local meteorological conditions and relevant comments. The survey findings are summarized in Table 2, and listings of the half-hour concentrations of selected PAHs in Table 3.

Note that the concentrations quoted in Table 2 which present the odour fingerprints are only estimates (within a factor of 5) since on-site calibrations were not performed except for the target PAH compounds. Also, the compound identities are tentative since they are based on single mass spectral interpretations. Isomers of dicyclic and tricyclic aromatic hydrocarbons, along with some physical characteristics, are listed in Appendix B. In Table 3 all 25 half-hour average concentrations for four PAH groups are reported. PAH levels were determined during various times of the day and night mainly in the residential area west of Ft. William/Water St. (See Map 1). The concentrations listed for the PAH groups refer to the sum of the concentrations due to different isomers involved.

June 10

This was a sunny, warm day with ENE-SE winds of up to 10 km/hr. In the morning, plume tracking was performed for PAHs downwind of NWP. A mild tar odour was noted while driving the mobile TAGA over the bridge on Central Avenue, west of the NWP property. Three consecutive fingerprints (nos. 01, 02, 03, Table 2) were recorded on Central Avenue, 100 m west of Maureen Street (Site A), during 10:56 to 12:23 hours. Analysis of these fingerprints revealed the presence of toluene, alkyl-benzenes, benzaldehyde, cresols, dibutylamine and four PAH groups in an estimated concentration range of less than 1 to 20 $\mu g/m^3$. A half-hour average of the four selected PAH groups was initiated at 12:29 hours (S01, Table 3). The wind direction was varying from NNE to ESE, the odour was intermittent and consequently the PAH levels were not constant. The average ambient level of naphthalene was 11 $\mu g/m^3$, about three times lower than the Ministry guideline, but instantaneous readings were as high as 48 $\mu g/m^3$. Note that retort #1 was opened and treated wood was taken out at 12:55 hours. For about one hour, due to continuing wind shifts, the tar odour was mild to strong. The TAGA was then positioned in the parking lot of NWP near the main entrance (Site B), at the end of Maureen Street and a fingerprint (no. 04, Table 2) was recorded while tar odours were constantly present. Note that at 13:20 hours retort #2, located approximately 400 m from the TAGA, had been opened; tar odours were strong, especially near a pile of previously treated railway ties. In addition to the compounds contained in fingerprint 01, 02 and 03, fingerprint 04 showed low levels of phenol, $C_{13}H_{14}$ and $C_{14}H_{10}$ PAH groups. Naphthalene was the most prominent compound at an estimated concentration of 30 $\mu g/m^3$. Upwind monitoring and PAH calibrations were performed in the parking lot of Environment Canada near Main Street and 110th Avenue starting at 14:57 hours.

June 11

Sunday, June 11, was a warm, sunny day with brisk E-ENE winds. Early in the morning the mobile unit was used to plume track in the area west of NWP; low levels of PAHs were detected at a distance of about 2 km downwind of the plant. Odours were absent even close to NWP property. The TAGA was calibrated for naphthalene, methylnaphthalene, biphenyl and fluorene upwind of NWP in the parking lot of Environment Canada. Background levels were also established at this site.

Following background sampling, plume tracking for PAHs was conducted near NWP; the PAH levels increased at the intersection of Maureen Street and Central Avenue. Strong tar odours were noted at the end of Maureen Street, in front of NWP's main entrance. The mobile unit was positioned in the NWP parking lot (Site B), 20 m from a pile of treated black ties, where the tar odours were even stronger. Mass spectral analysis of the ambient air (Fingerprint no. 05, Table 2) revealed the presence of seven PAH groups. Examples of possible PAH isomers are given in Table 2. Appendix B lists isomers from C_{10} up to C_{14} PAH groups, together with a few physical properties. The PAH levels from fingerprint 05 were estimated to be in the range 2 to 40 $\mu g/m^3$. Naphthalene was at 40 $\mu g/m^3$, methylnaphthalene and biphenyl levels were about four times lower, ethylnaphthalene was ten times lower and levels of fluorene, trimethylnaphthalene and anthracene were 2 to 3 $\mu g/m^3$.

At noon, winds started to shift from E to NE, odours were fading away, so the TAGA was moved to Maureen Street, south of the railway spur, north of the CNR bridge (Site C). This location was just south of the NWP property. Two half-hour average levels of PAHs were recorded (S02 and S03, Table 3); concentrations of naphthalene, methylnaphthalene, biphenyl and fluorene were 50, 13, 17 and 5.4 $\mu g/m^3$, and 42, 11, 14 and 4.7 $\mu g/m^3$. Instantaneous concentrations for naphthalene were as high as 150 $\mu g/m^3$. Wind shifts from ENE to ESE were noticed and a different type of odour was apparent, presumably emissions from nearby grain storage warehouses. A fingerprint (no. 06, Table 2) was recorded at 13:49 hours and only low levels of toluene, phenol, dibutylamine and naphthalene were detected. Later in the afternoon, PAH calibrations and background sampling was conducted upwind of NWP, near Main Street and 110th Avenue. Exploration of the NWP wood yard revealed that the nearby railway ties were evolving strong tar odours; no visible emissions were noticed during monitoring. According to the information about NWP wood treatment operations, provided by MOE Regional officers after the survey, the retort cylinders were not opened on June 11. Therefore, previously treated ties were the likely source of the compounds detected.

June 12

June 12 was a cool, cloudy day with ENE winds. Two half-hour average levels of four PAH groups were acquired in the parking lot of Thunder Bay Transit, just east of Ft. William, approximately two km from NWP (Site D). Moderate tar odours were present. Average ambient concentrations of the PAHs monitored are shown in Table 3 (S04, S05). The wind speed was steadily increasing and tar odours were noticeable. A fingerprint (no. 07, Table 2) was recorded at 11:20 hours at this site and the most abundant compound detected was naphthalene at an estimated level of 15 $\mu g/m^3$; note that the concentration from the two half-hour averages was 22 $\mu g/m^3$. Concentration estimates of nine more compounds, tentatively identified, are also listed in Table 2. Upwind monitoring was conducted in the parking lot of Prince Arthur Landing, north of NWP. Unfortunately, shortly after the completion of background monitoring and calibration procedures at 14:15 hours, it started to rain and sampling was halted for the day. The rain stopped the next day, late in the afternoon. Mobile sampling resumed on June 14.

June 14

This was a sunny day with brisk easterly winds. Plume tracking in the morning indicated that naphthalene levels in the residential area west of Ft. William were in the range 5 to 20 $\mu g/m^3$ correlating with the odours noted by the survey crew. Upwind monitoring and calibrations were performed in the parking lot of Prince Arthur Landing. A half-hour average (S06, Table 3) of PAH levels was recorded at noon in the parking lot of the Weldinghouse building located near John Street and Water Street (Site E). Due to wind direction variability, the tar odours were intermittent with intensities ranging from mild to moderate; the naphthalene level was 7.4 $\mu g/m^3$.

In the afternoon, treated wood was removed from retort #1 at 17:30 hours and from retort #2 at 18:35 hours. A member of the survey crew near the retorts made the following observations: treated wood on 16 carts with 45 ties on each, removed from retort #1, was steaming for more than one hour and odours were strong. Odours were stronger when treated wood was removed from retort #2. A half-hour average (S07, Table 3) of PAH levels was recorded at 17:58 hours near Ft. William and Water Street (Site F); odours were not strong. Plume tracking was conducted in the residential area west of Ft.

William for establishing a better downwind location. A plume tracking profile, measured in the time period 19:01-19:26 hours, is shown in Figure 1. The highest PAH levels were recorded along Ontario Street, between First Avenue and Second Avenue; naphthalene levels were close to 30 $\mu g/m^3$. Two half-hour average (S08 and S09, Table 3) PAH levels and a fingerprint (08, Table 2), measured at site G, indicated that naphthalene concentrations were about 10 $\mu g/m^3$. During the first ten minutes of the half-hour average designated S09 in Table 3, instantaneous naphthalene levels of up to 55 $\mu g/m^3$ were recorded. Low levels of toluene, alkyl benzenes and benzaldehyde were also detected. The TAGA response to PAH calibrations was examined once more upwind of NWP, and was similar to that established in the morning.

June 15

A half-hour average of PAH levels measured on Second Avenue, 50 m west of Ft. William (Site H), indicated total ambient PAH concentrations of 14 $\mu g/m^3$ with naphthalene being the most abundant at 8 $\mu g/m^3$. Instantaneous naphthalene levels of 50 $\mu g/m^3$ were detected, while plume tracking, near the NWP main entrance at the end of Maureen Street. A fingerprint (09, Table 2) was taken at site C but due to wind shifts levels of the detected compounds were low. Moderate tar odours were evident near Water Street and John Street. Two half-hour averages (S11 and S12, Table 3) of PAH levels and three fingerprints (10, 11 and 12, Table 2) were recorded in the parking lot of the Weldinghouse building (Site E) in the time period 12:45-14:32 hours. The highest half-hour average concentration of naphthalene was 19 $\mu g/m^3$. During this monitoring period all activities in the NWP wood treatment area were observed by a member of the survey crew: at 12:04 hours the door of retort #1 was opened, vast amounts of steam appeared, the treated wood was removed and, tar odour intensity increased dramatically. The retort #2 was opened at 13:00 hours and odours were again very strong near the pile of the freshly treated, steaming wood. For the first time retort #3 (wood treatment with pentachlorophenol - PCP) was opened and loaded with 12-foot long ties; neither emissions nor phenolic odours were noted.

Background levels were established in the parking lot of Environment Canada near Main Street and 110th Avenue. Following upwind monitoring plume tracking revealed the presence of PAHs and strong tar odours between Water Street and Vigars Street, about 100 m south of Bay Street approximately 1.5 km from NWP's retorts (Site I). Two half-hour averages (S13 and S14, Table 3) were recorded at this location. The first, at 17:13 hours, showed half-hour average concentrations of 52 $\mu g/m^3$ for naphthalene, 44% above the Ministry guideline. The maximum instantaneous concentration for naphthalene was 150 $\mu g/m^3$ for this monitoring period. The second, at 18:10 hours, showed average concentrations of 16 $\mu g/m^3$ for naphthalene. However note that the wind had shifted from ESE to SSE. A fingerprint (13, Table 2) was also measured at this site; concentrations of the tentatively identified compounds are in the range 1-15 $\mu g/m^3$. Winds kept shifting; consequently no further monitoring was carried out on this day.

June 16

Background levels were established in the morning, in the parking lot of Prince Arthur Landing. Because of wind shifts, calibrations of PAH target compounds were performed in the parking lot of Environment Canada. Monitoring was performed downwind of NWP near Court Street and Ft. William (Site J) in the time period 12:09-13:51 hours. A half-hour average of PAHs (S15, Table 3) showed naphthalene at 15 $\mu g/m^3$ with instantaneous concentrations of about 35 $\mu g/m^3$. With the odour still present, a fingerprint (no. 14, Table 2) was recorded. The most abundant compounds were toluene, benzaldehyde, phenol and naphthalene at levels in the range of 6-9 $\mu g/m^3$. Methyl phenol and alkyl-benzenes were also detected at levels not exceeding 2 $\mu g/m^3$. A second half-hour average (S16, Table 3) at site J showed lower naphthalene levels.

Later in the afternoon, strong tar odours were noted on Court Street between Ft. William and John Street (Site K). Three consecutive half-hour averages (S17, S18, S19) were recorded; concentrations of the four target PAH groups are listed in Table 3. Throughout this monitoring period, moderate to strong tar odours were present. While monitoring, observations of the activities near the NWP retorts were made by a member of the survey crew. The door of retort #1 was opened at 17:12 hours, considerable amounts of emissions were visible and four minutes later treated railway ties were pulled out. The half-hour average designated S18 in Table 3 was initiated at 17:15 hours. Approximately ten minutes later the TAGA, positioned at site K, recorded ambient naphthalene levels reaching 60 $\mu g/m^3$. The concentration profiles are shown on the left part of the composite diagram of Figure 2; the maxima occurred when the odour was quite strong approximately 10 minutes after treated wood was removed from retort #1. A few minutes later small wind shifts were observed, odours diminished and PAH concentration levels dropped significantly. At 18:00 hours retort #2 was opened and three minutes later treated wood was removed for open air drying. While the freshly treated ties from both retorts were still steaming, the half-hour average (S19) shown on the right of Figure 2 was measured. The average naphthalene concentration was 17 $\mu g/m^3$ with maximum instantaneous levels approaching 30 $\mu g/m^3$.

Two fingerprints (15 and 16, Table 2) and a half-hour average (S20, Table 3) of ambient PAH levels were recorded in the parking lot of the Weldinghouse building near Water Street and John Street (Site E). Benzaldehyde, toluene, naphthalene, alkyl-benzenes and methyl phenol were the most abundant compounds. Methyl phenol was just over the odour threshold of 4.4 $\mu g/m^3$. Background levels were established and the response of the TAGA to PAHs was examined once more at 20:00 hours in the parking lot of Environment Canada; compared with the morning's calibrations variations of less than 10% were observed.

June 17

Tar odours were noted near Central Avenue and Maureen Street. Odours were stronger along the CNR access route. A half-hour average (S21, Table 3) was recorded west of NWP, on CNR property, about 50 m east of Ft. William and 100 m from Maureen Street (Site L). Initially tar odours were present and naphthalene levels were fairly constant at 20 $\mu g/m^3$. Twenty minutes later a saw-dust odour was noted and, the level of naphthalene decreased abruptly. Mild to moderate tar odours were detected near Ontario Street and First Avenue (Site M). Two half-hour averages (S22 and S23, Table 3) were recorded indicating ambient naphthalene levels of 17 and 8.5 $\mu g/m^3$.

At 13:24 hours the mobile TAGA was moved to the parking lot of Environment Canada for background monitoring and calibrations since no activities in the NWP wood treatment area were apparent. According to NWP schedule provided by MOE Regional officers, retort #3, which uses PCP, was opened the previous night at 00:25 hours, retort #2 at 13:25 hours and retort #1 at 13:50 hours and treated wood was removed. At 15:50 hours a half-hour average (S24, Table 3) for PAH levels was initiated near Water Street and John Street (Site E) where tar odour intensities were moderate to strong; naphthalene levels averaged to 14 $\mu g/m^3$. The other three PAH groups showed levels in the range 1.7 to 5.2 $\mu g/m^3$. A second half-hour average (S25, Table 3) was recorded one hour later; compared with the first, PAH average concentrations were similar. Tentatively identified pollutants from fingerprint (no. 07) taken at this site, are shown in Table 2 along with corresponding estimated concentrations. Chlorophenols were not detected; but note that the monitoring was performed several hours after wood treated with PCP was removed from retort #3.

4.0 Summary and Conclusions

The mobile TAGA 3000 unit conducted an air monitoring survey in Thunder Bay, Ontario on June 10, 11, 12, 14, 15, 16 and 17 at the request of the Ministry's Northwestern Region. The purpose of this survey was to attempt to fingerprint the odours associated with Northern Wood Preservers Inc. and to determine ambient levels of phenols, chlorophenols and PAHs downwind of this plant. The findings of this survey are summarized by the following points:

1) Tar-type odours were recognizable downwind of NWP. The odours were generally strongest near the plant property. The odours were moderate to strong at times

in residential areas west of NWP. Strong odour episodes occurred primarily when freshly treated wood was removed from either creosote retort #1 or creosote retort #2. Such odour episodes coincided with enhancement of the four PAH groups ($C_{10}H_8$, $C_{11}H_{10}$, $C_{12}H_{10}$, $C_{13}H_{10}$) as recorded downwind of NWP by the mobile TAGA 3000. A few of the compounds which were detected (eg. methyl phenol, biphenyl, methylnaphthalene) and have low odour thresholds, may have contributed to the odour present in the vicinity of NWP.

2) Although phenolic odours were not evident, possibly because tar odours were masking them, phenol and cresol were detected. Concentration estimates of phenol are in the range non-detected to 9 $\mu g/m^3$ and, of cresol non-detected to 5 $\mu g/m^3$ which are well below the Ministry standards of 100 and 230 $\mu g/m^3$. Chlorophenols were not detected during any of the monitoring periods. However, wood treatment with pentachlorophenol only occurred once during this survey. This was early morning (00:25 hours) of June 17, 1989, and the TAGA 3000 was in a recycle mode.

3) Mass spectral analysis of the odours downwind of NWP indicated the presence of toluene, phenols, alkyl-benzenes, dibutylamine, benzaldehyde and volatile PAHs. Naphthalene, methylnaphthalene, biphenyl, ethylnaphthalene, fluorene, trimethyl naphthalene and anthracene are isomers which may have contributed to the ambient levels of the PAH groups detected. Estimated concentrations based on fingerprint data (See Table 2) ranged from non-detected to 40 $\mu g/m^3$.

4) The most abundant contaminant was naphthalene. Quantitative half-hour averages (See Table 3) indicated that its concentration ranged from 7.4 to 52 $\mu g/m^3$ with instantaneous maxima as high as 150 $\mu g/m^3$. The Ministry guideline, which is based on health effects, is currently set at 36 $\mu g/m^3$ for a half-hour average concentration. Only 3 of 25 half-hour averages exceeded the MOE guideline. The TAGA can only detect volatile compounds; other PAHs may also be present in the ambient air in the form of particulates or aerosols.

In conclusion, the survey results indicated that volatile PAH compounds (two and three member rings) and, to a lesser extent, phenols and cresols are partially responsible for the wood preserving odours observed downwind of NWP. It is important to note that these pollutants were detected near the plant property as well as in residential areas west of it. It should be mentioned that of the contaminants detected in the residential areas, only naphthalene was present in levels comparable to existing Ministry guidelines or standards. The highest half-hour ambient level of naphthalene was 52 $\mu g/m^3$, whereas the Ministry guideline for naphthalene is 36 $\mu g/m^3$. Three of the half-hour averages exceeded this Ministry guideline. It may be of interest to note that the guideline for naphthalene is based on health effects. The Ministry of the Environment has set a guideline for byphenyl, 60 $\mu g/m^3$, which is based on odours. The maximum half-hour average concentration of biphenyl recorded during this survey was 17 $\mu g/m^3$. There is no Ministry standards or guidelines for the other PAHs. It is suggested that the Northwestern Region consider the implementation of a detailed PAH monitoring programme in the vicinity of NWP to determine the impact of PAHs on the local air quality.

5.0 Acknowledgements

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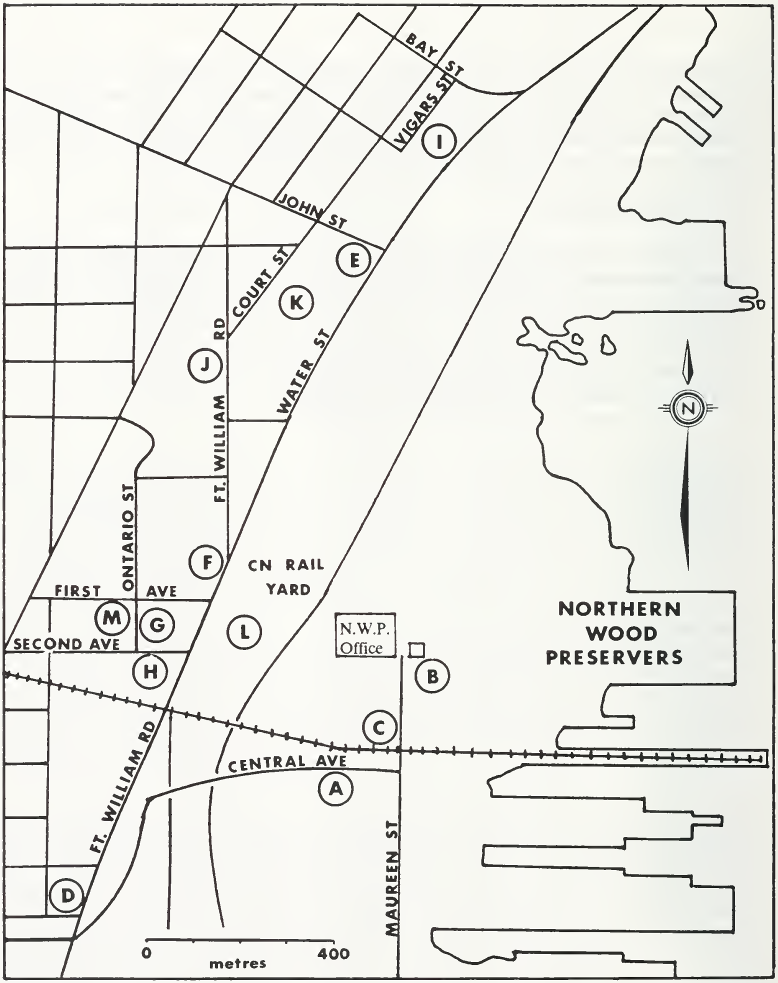


Map 1: Monitoring Locations Downwind of Northern Wood Preservers Inc.

Table 1: Mobile TAGA 3000 Monitoring Periods and Locations
Thunder Bay (Northern Wood Preservers Inc.) Survey 1989

Date	Fingerprint Number	Monitoring Period	Location[1]	Meteorological Conditions[2] AT	WS	WD	Comments
Jun 10	01	10:56-11:21	A	16	00-10	ENE	Tar and lumber odour present
	02	11:24-11:36	A	15	05-10	ENE	Tar and lumber odour present
	03	11:57-12:23	A	18	00-10	E	Strong tar odour, winds variable
	04	13:56-14:08	B	25	05-10	SE	Strong tar odour (On plant property)
Jun 11	05	11:41-12:04	B	19	05-10	ENE	Moderate to strong tar odour (On plant property)
	06	13:49-14:01	C	23	00-10	ENE	No odours, winds variable
Jun 12	07	11:20-11:30	D	12	15-20	ENE	Moderate tar odours
Jun 14	08	20:06-20:24	G	13	05-10	E	Faint odour present
Jun 15	09	11:44-11:50	C	18	00-05	ESE	Faint tar odour present
	10	13:18-13:37	E	15	05-15	E/ESE	Tar odour present
	11	13:43-13:47	E	17	05-10	E	Moderate odour present
	12	14:30-14:32	E	18	05-10	ENE	Tar odour present
	13	17:50-18:01	I	19	10-15	SE	Odour present
Jun 16	14	12:46-13:05	J	18	00-10	ESE	Faint tar odour present
	15	18:43-19:06	E	20	00-10	ESE/ENE	Faint tar odour present
	16	19:42-19:46	E	20	00-05	E	Faint tar odour present
Jun 17	17	16:21-16:37	E	22	15-20	SE	Mild to moderate odour present

Notes:
1. See Map 1 for sampling locations.
2. Met. conditions at 10 metres: AT=ambient temperature (°C); WS=range of wind speeds (km/hr); WD=predominant wind direction

Table 2: Mobile TAGA 3000 Odour "Fingerprints"

Target Source: Northern Wood Preservers Inc.
Thunder Bay Survey 1989

Compounds Detected[1]	Estimated Concentrations[3] ($\mu g/m^3$)										
Fingerprint[2] #=	01	02	03	04	05	06	07	08	09	10	11
toluene	9	2	4	6	3	2	3	3	ND	2	4
phenol	ND	ND	ND	9	ND	5	ND	ND	ND	4	ND
xylenes	3	2	5	2	ND	ND	3	2	ND	2	3
benzaldehyde	20	6	8	2	4	ND	5	5	2	2	8
methyl phenol	4	1	2	1	2	ND	2	1	1	1	2
C_3-alkyl benzenes	2	1	3	2	ND	ND	3	2	ND	1	2
dibutylamine	1	3	1	3	8	4	1	1	ND	ND	2
PAHs[6]:											
$C_{10}H_8$ (eg. naphthalene)	4	1	10	30	40	2	15	9	2	4	15
$C_{11}H_{10}$ (eg. methylnaphthalene)	1	ND	2	5	9	ND	3	1	ND	1	3
$C_{12}H_{10}$ (eg. biphenyl)	1	ND	1	4	8	ND	1	1	ND	ND	2
$C_{12}H_{12}$ (eg. ethylnaphthalene)	ND	ND	1	2	4	ND	1	ND	ND	ND	1
$C_{13}H_{10}$ (eg. fluorene)	ND	ND	ND	2	3	ND	ND	ND	ND	ND	ND
$C_{13}H_{14}$ (eg. trimethylnaphthalene)	ND	ND	ND	1	2	ND	ND	ND	ND	ND	ND
$C_{14}H_{10}$ (eg. anthracene)	ND	ND	ND	3	3	ND	ND	ND	ND	ND	ND

(Table 2 continued...)

Table 2: Mobile TAGA 3000 Odour "Fingerprints"
Target Source: Northern Wood Preservers Inc.
Thunder Bay Survey 1989

Compounds Detected[1]	Estimated Concentrations[3] ($\mu g/m^3$)						Ministry	Odour
Fingerprint[2] #=	12	13	14	15	16	17	Criteria[7]	Threshold[8]
toluene	4	15	9	15	8	5	2,000 (s)	7,000[b]
phenol	ND	9	8	ND	ND	7	100 (s)	22[b]
C_2-alkyl benzenes[4]	5	2	ND	6	2	3	2,300 (s)	3,600[a]
benzaldehyde	15	6	9	20	7	3	n/a	4,300[b]
methyl phenol	4	2	2	5	2	1	230 (s)	4.4[b]
C_3-alkyl benzenes[5]	3	2	1	5	2	1	n/a	n/a
dibutylamine	1	1	1	1	1	ND	n/a	1,400[b]
PAHs[6]:								
$C_{10}H_8$ (eg. naphthalene)	10	5	6	15	7	6	36 (pg)	450[a]
$C_{11}H_{10}$ (eg. methylnaphthalene)	3	1	1	2	1	1	n/a	20[b]
$C_{12}H_{10}$ (eg. biphenyl)	1	1	1	1	1	1	60 (g)	60[b]
$C_{12}H_{12}$ (eg. ethylnaphthalene)	1	ND	ND	1	ND	ND	n/a	250[b]
$C_{13}H_{10}$ (eg. fluorene)	ND	ND	1	ND	ND	ND	n/a	n/a
$C_{13}H_{14}$ (eg. trimethylnaphthalene)	ND	ND	ND	ND	ND	ND	n/a	n/a
$C_{14}H_{10}$ (eg. anthracene)	ND	ND	1	ND	ND	ND	n/a	n/a

Notes:

1. Tentative identities based on interpretation of APCI/MS mass spectral data. Numbers in parentheses indicate ion mass in atomic mass units (amu)
2. See Table 1 for sampling locations and monitoring periods
3. Two-minute averaged concentrations (estimated ±5x). ND = not detected
4. C_2-alkyl benzenes: mixture of xylene and ethyl benzene. Odour threshold value refers to mixed xylenes
5. C_3-alkyl benzenes: mixture of propyl benzene, ethyl toluene and trimethyl benzene
6. See Appendix B for a list of isomeric PAH compounds including some of their physical properties
7. In $\mu g/m^3$, (s) = O.R. 308 Standard; (pg) = Provisional Guideline; (g) = guideline
8. In $\mu g/m^3$, population perception threshold

a. Procedure for the determination of odour impact models by the binary port odour panel method. Ontario Ministry of the Environment, Report # AMP-143 (Feb '89), Draft # 10

b. Gemert van, L.J., Central Institute for Nutrition and Food Research TNO), Netenbreizer, A.H., (National Institute for Water Supply), Compilation of odour threshold values in air and water, Netherlands, 1977

Table 3: Mobile TAGA 3000 PAH Concentrations (1/2 Hour Ave.)

Thunder Bay (Northern Wood Preservers Inc.) Survey 1989

Date	Sample Number	Start Time	Location[1]	Meteorological Conditions[2] AT	WS	WD	1/2 Hour Ave. Conc.[3] ($\mu g/m^3$) $C_{10}H_8$	$C_{11}H_{10}$	$C_{12}H_{10}$	$C_{13}H_{10}$	Comments
Jun 10	S01	12:29	A	18	00-10	NNE/ESE	11	2.9	3.2	1.0	Faint intermittent odour
Jun 11	S02	12:35	C	20	05-10	ENE	50	13	17	5.4	Tar odour present
	S03	13:12	C	20	05-10	ENE	42	11	14	4.7	Moderate tar odour
Jun 12	S04	10:03	D	13	10-25	ENE	22	4.6	4.0	1.0	Moderate tar odour
	S05	10:34	D	12	20-30	ENE	22	5.1	5.0	1.2	Moderate tar odour
Jun 14	S06	11:55	E	11	05-15	SSE	7.4	1.8	2.0	0.6	Moderate odour Winds variable
	S07	17:58	F	12	05-10	E	10	2.9	2.9	0.9	Tar odour present
	S08	19:25	G	13	05-10	E	11	3.3	3.3	1.0	Faint tar odour
	S09	20:37	G	11	05-10	ENE	10	1.8	1.3	0.3	Strong odour present
Jun 15	S10	10:34	H	16	05-10	E	8.2	1.9	2.5	0.9	Faint odour present
	S11	12:45	E	17	05-15	ESE	19	5.4	5.8	1.5	Mod. to strong odour
	S12	13:51	E	16	05-10	E	12	2.6	2.4	0.6	Mod. to strong odour
	S13	17:13	I	19	10-15	ESE	52	15	10	2.2	Strong tar odour
	S14	18:10	I	19	05-15	SSE	16	4.3	4.9	1.5	Woody/tar odour

(Table 3 continued...)

Table 3: Mobile TAGA 3000 PAH Concentrations (1/2 Hour Ave.)

Thunder Bay (Northern Wood Preservers Inc.) Survey 1989

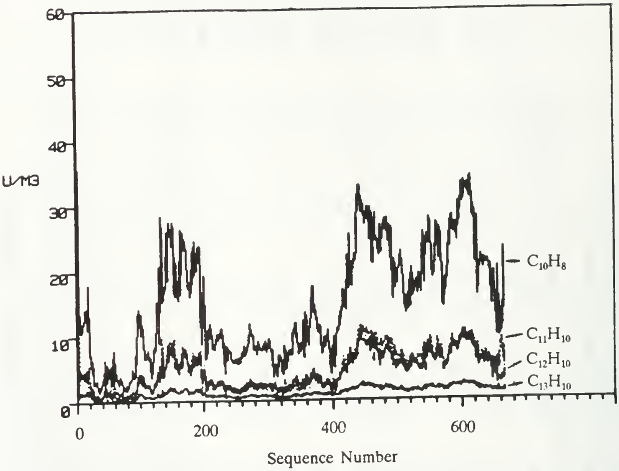
Date	Sample Number	Start Time	Location[1]	Meteorological Conditions[2]			1/2 Hour Ave. Conc.[3] ($\mu g/m^3$)				Comments
				AT	WS	WD	$C_{10}H_8$	$C_{11}H_{10}$	$C_{12}H_{10}$	$C_{13}H_{10}$	
Jun 16	S15	12:09	J	17	05-10	E	15	4.6	3.5	1.3	Moderate tar odour
	S16	13:51	J	18	05-15	E	9.7	3.7	3.8	1.3	Faint to mod. odour
	S17	16:45	K	20	05-10	ENE	22	4.8	3.6	1.2	Mod. to strong odour
	S18	17:15	K	21	10-15	ENE	13	3.5	3.0	0.9	Tar odour present
	S19	17:54	K	18	00-10	ENE	17	4.7	4.7	1.6	Moderate tar odour
	S20	19:11	E	20	00-05	E	16	3.6	3.2	1.0	Moderate tar odour
Jun 17	S21	10:24	L	19	05-10	ENE	13	4.4	4.7	1.6	Mod. wood/tar odour
	S22	12:21	M	24	00-05	E	17	4.9	5.8	2.1	Faint tar odour
	S23	12:54	M	25	00-05	E	8.5	2.2	3.1	1.0	Faint to mod. odour
	S24	15:50	E	23	10-20	SE	14	3.2	5.2	1.7	Mod. to strong odour
	S25	16:42	E	22	15-20	SE	14	3.7	6.1	1.9	Mod. wood/tar odour

Note: 1. See Map 1 for monitoring locations.

2. Met. conditions at 10 metres: AT=ambient temperature (°C); WS=range of wind speeds (km/hr); WD=predominant wind direction.

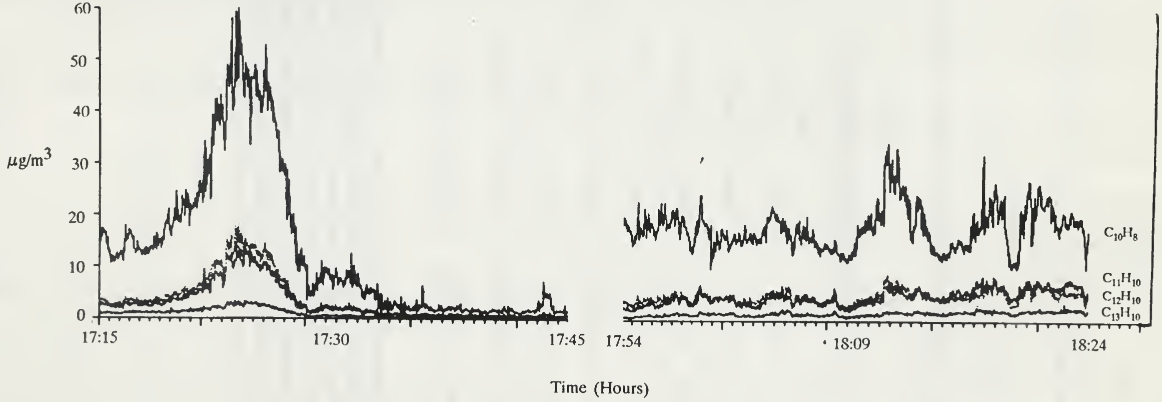
3. ± uncertainty of quoted concentrations based on multiple daily calibrations of PAHs (eg. $C_{10}H_8$ = naphthalene, $C_{11}H_{10}$ = methylnaphthalene, $C_{12}H_{10}$ = biphenyl and $C_{13}H_{10}$ = fluorene) is in the range 2 to 5%. See Appendix A for daily calibrations and Appendix B for isobaric and isomeric PAH compounds including some of the physical properties

Figure 1: Plume Tracking of Selected PAH Groups Downwind of Northern Wood Preservers on June 14, 1989



Flag	Sequence No.	Instantaneous Concen ($\mu g/m^3$)				Location
		$C_{10}H_8$	$C_{11}H_{10}$	$C_{12}H_{10}$	$C_{13}H_{10}$	
A	11	12	4	4	1	Ft. William & Second Ave.
B	27	3	1	1	ND	Thunder Bay Transit
C	41	3	1	1	ND	Ft. William & Sixth Ave.
D	55	3	1	1	ND	High St. & Sixth Ave.
E	69	3	1	2	ND	High St. & Fifth Ave.
F	81	2	1	1	ND	High St. & Fourth Ave.
G	95	9	2	3	1	High St. & Third Ave.
H	107	7	2	2	1	High St. & Second Ave.
I	136	25	7	7	1	Ontario St. & Second Ave.
J	154	27	9	8	2	Ontario St. & First Ave.
K	179	18	5	5	1	High St. & First Ave.
L	189	21	6	6	2	High St. & Second Ave.
M	204	6	2	2	1	High St. & Third Ave.
N	326	8	3	2	ND	Memorial & Fourth Ave.
O	343	12	2	4	1	Memorial & Third Ave.
P	352	8	2	3	1	High St. & Third Ave.
Q	368	14	3	3	1	High St. & Second Ave.
R	399	5	1	2	ND	Ontario St. & Second Ave.
S	422	15	4	5	1	Ontario St. & First Ave.
T	625	28	8	7	2	Ontario 100m S. of First
U	664	15	7	3	1	Ontario 100m S. of First

Figure 2: Real-time Measurements of Four PAH Groups Downwind of Northern Wood Preservers at Site K, June 16, 1989



Note: 1. The door to Retort #1 (North Retort) opened at 17:12 hours and the treated wood was removed at 17:14 hours
2. The door to Retort #2 (Middle Retort) opened at 18:00 hours and the treated wood was removed at 18:02 hours
3. See Table 3 (S18, S19) for half-hour average PAH concentrations and relevant comments.

Appendix A

Calibration[1] of PAHs[2]: Naphthalene ($C_{10}H_8$), 2-methylnaphthalene ($C_{11}H_{10}$), biphenyl ($C_{12}H_{10}$) and fluorene ($C_{13}H_{10}$).

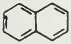
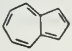
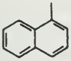
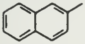
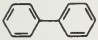
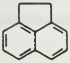
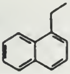
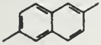
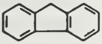
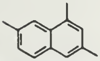
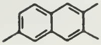
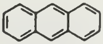
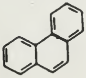
Slopes of response curves (ICPS/μgm^{-3})

Date	$C_{10}H_8$	$C_{11}H_{10}$	$C_{12}H_{10}$	$C_{13}H_{10}$	# Tcals	R2[4]
Jun 10	1,761	1,432	893	1,128	1	
Jun 11	1,563±3%[3]	1,212±4%	767±2%	931±2%	6	0.9928
Jun 12	1,959±4%	1,652±3%	1,018±4%	1,325±4%	3	0.9986
Jun 14	2,191±4%	1,897±8%	1,231±6%	1,503±7%	6	0.9998
Jun 15	1,593±4%	1,292±6%	752±7%	902±6%	3	0.9911
Jun 16	2,011±6%	1,677±4%	1,020±4%	1,265±6%	5	0.9971
Jun 17	1,498±3%	1,196±3%	713±3%	837±3%	3	0.9957

1. Calibrations were performed upwind of Northern Wood Preservers Inc.
2. A mixture of naphthalene, 2-methylnaphthalene, biphenyl and fluorene was used.
3. The standard deviation is based on the number of daily calibrations(# Tcals).
4. Average correlation coeficients of linear plots of response (ICPS) vs PAH concentration ($\mu g/m^3$). The lowest value of R2 was 0.9822 and the highest 1.0000. Calibrations were performed in the concentration range 0 to 60 $\mu g/m^3$ for naphthalene and biphenyl, 0 to 120 $\mu g/m^3$ for 2-methylnaphthalene and 0 to 25 $\mu g/m^3$ for fluorene.

Appendix B

List of Polycyclic Aromatic Hydrocarbons (PAHs), Their Structure, Molecular Weight, Melting and Boiling Points

Structure	IUPAC nomenclature	Molecular weight	Melting point (°C)	Boiling point (°C)^{760}
	Naphthalene	128 19	81	218
	Azulene	128 19	100	270
	1-Methylnaphthalene	142 20	-22	245
	2-Methylnaphthalene	142 20	35	241
	Biphenyl	154 21	71	255
	Acenaphthene	154 21	96	279
	1-Ethylnaphthalene	156 23	-14	259
	2,6-Dimethylnaphthalene	156 23	110	262
	Fluorene	166 23	117	294
	1,3,7-Trimethylnaphthalene	170 25	14	280
	2,3,6-Trimethylnaphthalene	170 25	101	286
	Anthracene	178 24	216	340
	Phenanthrene	178 24	101	338

Appendix C

Northern Wood Preservers Inc.
Thunder Bay

Introduction:

Northern Wood Preservers Inc., the third largest sawmill in Ontario, is located on the shoreline of Lake Superior, in the City of Thunder Bay. The site is well served by transportation, being accessible by water via Thunder Bay Harbour, by rail via CNR and CPR, and by road via Maureen Street.

The Northern Wood Preservers Inc. complex includes a slasher, a tie sawmill, a lumber sawmill, three drying kilns, a chromated copper arsenate (CCA) treatment plant. A comprehensive materials handling system is required in order to move wood between these operations, and subsequently to market.

Wood Processing:

Slashed roundwood feed to the sawmill is passed through a hot pond (log soaking pit), the purpose of which is to remove ice or grit which could damage saw blades, and to loosen the bark in order to facilitate debarking. Sawmill dimensional lumber is kiln dried, and ties are either kiln or air dried.

Dried dimensional lumber is fed to the planer mill, and is either marketed as dressed lumber, or is further processed by chromated copper arsenate (CCA) treatment.

Utility poles, railway ties and a small amount of miscellaneous timbers and guard rail posts are treated with creosote or pentachlorophenol.

There are two areas used for wood preserving: a treatment facility that uses only chromated copper arsenate, and a three retort treatment area, in use since 1935, where wood is treated with creosote (two retorts) and pentachlorophenol (one dedicated retort).

The Wood Preserving Process:

The treatment cycle employed when using creosote or pentachlorophenol is dependent upon both the moisture content of the wood and the species of wood to be treated. In general, however, the treatment cycle would consist of:

The wood to be treated is securely fastened on metal trams, which are rolled into the retort on steel tracks. When a charge of loaded trams has been placed in the retort for processing, the hinged door is closed and locked in place.

Steam seasoning is not considered a drying method, but it does remove up to 64 kg of water per cubic meter of wood, and makes the wood more permeable for treatment. Live steam at 115 to 118 °C is pumped into the retort, and pressure is applied to maximize the penetration of steam into the wood.

After steam seasoning is completed, a vacuum is placed on the retort cylinder and moisture laden air is removed to a contaminated condensate storage tank. Any condensate on the floor of the retort is drained off to this tank as well, where it is held for later treatment.

The cylinder is filled with the desired preservative, and approximately 1034 KPa of pressure at 87 °C is applied in order to ensure good penetration of the wood by the preservative. The temperature in the retort is increased to 99 to 102 °C, and the pressure is removed.

The wood is left in the preservative long enough to ensure that the pressure within the wood cells is in equilibrium with atmospheric pressure. This "expansion bath" ensures a minimum of bleeding from the treated wood once it is removed from the cylinder.

The preservative is pumped back into the working tank, and a vacuum is applied to the retort cylinder. All drainings are directed to the working tank, the door is opened and the trams rolled out onto the charge area for further handling.

Wastewater Treatment:

The wastewater discharged to the treatment plant is the condensate generated during steam conditioning of the wood in the retort, prior to the pressure treatment of the wood with preservative. The condensate contains water-soluble wood extractives, primarily carbohydrates. Because wood conditioning and treatment are carried out in the same retort, the condensate generated following treatment with creosote or pentachlorophenol is highly contaminated with these materials. This problem does not occur with CCA treatment, as the preservative is waterborne, and all condensates are recovered for further use.

The following is a list of the times when retort doors were opened following wood treatment at Northern Wood Preservers during our survey period. This information was provided to the Ministry's Regional Office by Northern Wood Preservers Inc.

Wood Treatment Operations June 10 - 17, 1989
Northern Wood Preservers Inc.

Charge	Date	Time of Retort Opening Retort #1 (Creosote)	Retort #2 (Creosote)	Retort #3 (PCP)
184	June 10	12:55		
185	June 10		13:20	
185	June 12		23:55	
186	June 12	16:50		
187	June 12		17:40	
188	June 13	2:30		
189	June 13	16:30		
190	June 13		17:10	
191	June 14	2:20		
192	June 14		3:10	
193	June 14	17:30		
194	June 14		18:35	
195	June 15	12:10		
196	June 15		13:00	
197	June 15	23:00		
198	June 16		24:20	
18	June 16			24:25
199	June 16	17:25		
200	June 16		18:30	
201	June 17	13:50		
202	June 17		13:25	